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13. ABSTRACT *(Maximum 200 words)*

Cadmium sulfide quantum dot materials are promising candidates for many nonlinear optical applications, because of their high third-order nonlinear susceptibilities. The UCLA teams has been collaborating with the University of Arizona and the Tokyo Institute of Technology in the fabrication and testing of such materials. Two processing techniques were used. The first one involved the preparation of a sodium borosillicate gel containing Cd salts. The gel was converted to dense glass at 550 degree and the Cd salt to CdS. The second one involved the use of Ormosil (organically modified silicate) as the matrix containing CdS microcrystals. A new method was developed to anchor the Cd salts onto the gel matrix so that subsequently, the CdS distribution in the matrix became highly uniform. Samples containing in excessof 10 wt.% of CdS were prepared with X(3) values up to 10-8 e.s.u. with practically no photodarkening effects. The sodium borosilicate glass samples were fabricated into channel waveguides by sodium to potasslum lon-exchange.

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June, 1993

1. Introduction and Background

The first phase of the present project was first initiated in October 1, 1987 and concluded on September 30, 1990. The original objective was to utilize a small team of international experts, to pool their knowledge and expertise, and thus to make it more efficient for the development of some superior electronic and optical materials. In particular, chemical processing of two families of relatively new materials was targeted for this collaborative program. These materials were (a) the superconducting ceramics and (b) the nonlinear optical nanocomposites. The original international team consisted of Professor J. Livage of the University of Paris, France, Professor A. Wright of Reading University, U.K., and Professor M. Yamane of the Tokyo Institute of Technology, Japan. Professor Livage would study the chemical reactions of sol-gel based liquid solutions for ceramic superconductors. Professor Wright would study the structures of amorphous gels. Professor Mackenzie would study the preparation of the superconducting ceramics from sol-gel solutions. Professor Yamane would collaborate with Professor Mackenzie on the preparation of quantum dot materials based on the suspension of ultrafine crystals of semiconductors in glassy matrices. Although the program had started in 1987, the collaborative work between Professors Yamane and Mackenzie only began in 1989. This first phase was successfully completed by September 30, 1990. A renewal proposal was submitted in 1990 for the continuation of this project. However, a long delay was experienced in the approval process. It was not until July, 1991 before formal approval was granted and the originally proposed research was severely cut back.

This second phase of the program officially commenced on July 15, 1991. The proposed research on ceramic superconductor was deleted. The research activities of this phase have been concerned only with nonlinear optical materials.

The only foreign collaborator has been Professor M. Yamane of the Tokyo Institute of Technology. From July 15, 1991 to May 14, 1992, Professor Yamane's support was in the form of travel funds between Japan and Los Angeles, plus living expenses for three weeks in Los Angeles where he came to UCLA for discussions. In the past year, the funding was expanded to permit one of Professor Yamane's assistants, a Dr. T. Takada, to spend one year at UCLA and one of our Ph.D. students, Ms. Lisa Kao to work at the Tokyo Institute of Technology. In addition, our collaboration with Professor N. Peyghambarian of the Optical Sciences Center, University of Arizona, has also been increased.

The international collaborative effort was then greatly enhanced. This second annual report summarizes the progress made in the past year.

2. Research on Semiconductor Quantum Dot Materials based on CdS

Semiconductor quantum dot materials based on CdS have been prepared via the sol-gel technique with sodium borosilicate glasses as well as Ormosils as the hosts. Both families of such materials have been shown to have high $\chi^{(3)}$ values of up to 6×10^{-7} esu. One of the most significant results obtained this year was the confirmation that the sol-gel derived sodium borosilicate glass samples were much less susceptible to photodarkening under laser irradiation than conventional melt derived glass samples. The experiments were performed at the Optical Sciences Center at Arizona by Professor N. Peyghambarian and his colleagues.

Quantum dots grown by the sol-gel process show drastically different characteristics in the photoinduced absorption behavior. Figures 1(a) and 1(b) show the differential absorption spectra of (a) the sample obtained by melt-quenching technique, and (b) the sol-gel derived samples, respectively. Solid and dashed curves are associated with the $\Delta\alpha L$ spectra taken by subtraction of the unpumped spectrum from the pumped spectrum. The sharp peak at 451 nm in (a) is due to scattering of the pump beam by the sample. The dominant characteristic in Figs. 1(a) and 1(b) is the decrease in the absorption (negative $\Delta\alpha L$ peak) resulting from bleaching of the exciton state. Very little change is observed in the nonlinear spectrum after extensive exposure (2 hours) to a pump laser with 5 μJ energy tuned at 451 nm for sample C. This is in direct contrast to the nonlinear spectrum obtained from the sample made by the melt-quenching technique [see Fig. 1(a)] which shows a reduction of $\Delta\alpha L$ by a factor of $\approx$ 20 as a result of photodarkening after similar pump exposure conditions. The difference in the photodarkening behavior of the samples may be attributed to the difference in the media surrounding the quantum dots (the difference of the surface ions), and the crystallinity of the quantum dots.

It is now well established that the $\chi^{(3)}$ values of quantum dot materials are dependent on the size of the CdS crystallites. It is obvious that the optimum performance of nonlinear optical samples will be dependent on the uniformity of the sizes of the CdS particles. In the past year, we have developed a new process to better control particle size distribution. In the sol-gel process, the particle size broadening of the quantum dots is attributed to the inhomogeneous distribution of Cd^{2+} ions and particle formation at different stages of sample preparation such as drying and heat-treatment. Figure 2-I shows that in the previous process for preparing CdS quantum dots in Na_2O-B_2O-SiO_2 glass and ORMOSIL, the Cd^{2+} ion distribution in the gel changes continuously throughout the various drying stages. Cd^{2+} salts dissolved in the liquid phase fill the pores of the wet gel as shown in Fig. 2-I(a). During drying, evaporation of the liquid phase gradually concentrates the salt solution. Figure 2-I(b) shows that upon reaching the solubility limit of the metal salt in the liquid phase, precipitation occurs on the pore walls of the wet gel. During heat-treatment under flowing oxygen gas, the salt particles [$Cd(OAc)_2$, $Cd(NO_3)_2$] are converted into CdO particles and may grow further as Cd^{2+} ions dissolved in the gel matrix diffuse to the site of the particles. The Cd^{2+} ions which are dissolved in the gel matrix may also nucleate and grow into CdO particles (Fig. 2-I(d). This phenomenon will cause further size broadening. The oxidized gels are then exposed to H_2S gas to convert cadmium oxide into sulfide. The final sulfidation process will have little effect on particle size if the reaction is carried out at low temperatures (<120°C).

One method to narrow the particle size distribution is to uniformly distribute the cadmium ions in the starting sol. This can be achieved by anchoring the cadmium ions to the gel matrix via a bifunctional ligand of an organically-substituted alkoxysilane. Several alkoxysilanes, Y---$Si(OR)_3$ (Y--- stands for $H_2N(CH_2)_3$, $H_2N(CH_2)_2NH(CH_2)_3$, $NC(CH_2)_3$, etc. amine-alkyl ligands) have been tested to link the metal complex moiety (L_nM). The bifunctional ligands consist of a group Y---capable of coordinating the LnM moiety and a hydrolyzable silyl group, separated by an inert spacer (---, such as propyl group). The complex, L_nM---$Si(OR)_3$, formed by simply mixing the metal moiety and the functional alkoxysilane in a solvent can be anchored to the silica gel matrix by the co-condensation reaction of the complex with silicon alkoxysilane, $Si(OR)_4$, via the sol-gel process as shown below:

$$L_nM\text{-}Y\text{---}Si(OR)_3 + Si(OR)_4 \xrightarrow{\text{cat./}H_2O} L_nM\text{-}Y\text{---}\overset{|}{\underset{|}{Si}}\text{-O-}\overset{|}{\underset{|}{Si}}\text{-}$$

Once the cadmium ions are anchored to the Si-O-Si network of the gel matrix, precipitation of the cadmium salts during drying is prevented, and a much narrower particle size distribution will be expected as shown in Fig. 2-II. After heat-treatment, the particles which are formed by the nucleation and growth are also expected to be smaller than those obtained by the previous method since the M-Y bonding prevents the diffusion of the cadmium ions.

Among the functional alkoxysilanes that have been tested in the preliminary experiments, 3-aminopropyl triethoxysilane $H_2N(CH_2)_3$ $Si(OC_2H_2)_3$, has been shown to be the most promising compound for controlling the particle size distribution of the quantum dots. Figure 3 shows the TEM micrographs of the newly developed gels using 3-aminopropyl triethoxysilane to control the CdO particle size distribution in the gels. Uniform and homogeneouslv dispersed CdO particles have been successfully prepared up to 13 wt.%. Figure 4 compares the CdS particle sizes and size distributions in the various gel samples. The CdS particle size distribution in the newly developed gels seem to be much narrower than in both the PDMS-TEOS Ormosil and sodium borosilicate gel samples. In addition, compared to the latter two types of gels, the particle sizes in the new gels with similar CdS concentration are much smaller. The linear absorption spectrum of Fig. 5 shows that the particle size in the improved gel is much smaller than that in the sodium borosilicate glass, since the absorption edge shifted towards much shorter wavelengths. Furthermore, improved particle size control has also been observed in the metal-cluster (Au) doped gel samples.

Samples of various thicknesses made by this new method have been sent to Professor Peyghambarian for $\chi^{(3)}$ measurements.

3. Research on Nonlinear Optical Materials based on Ultrafine Metal Clusters in ORMOSILS

Another family of ultrafine particles which, when dispersed in a glassy matrix, has been show to have high $\chi^{(3)}$ involves metal clusters. Because of the importance of obtaining scientific understanding of the differences of the origins of third-order nonlinear behavior and of the need to compare the properties of semiconductor-based samples with those containing metal clusters, we have also been investigating the preparation and properties of Au, Pt and Ag clusters in Ormosils. Two processes were used to form the metal clusters as shown in Fig. 6. The UV irradiation method was interesting in that metal clusters could be formed at room temperature. This suggested the possibility of pattern formation with the use of a mask. Figure 7 shows the results of the formation of letters in an Ormosil sample using the UV irradiation method. Three is a possibility that this technique can be exploited by industry for information storage. The preliminary mechanism is given below:

$$HAuC\ell_4 \xrightarrow{h\nu} Au^o + HC\ell + 3/2\, C\ell_2$$

$$nAu^o \longrightarrow (Au^o)_n$$

4. Publications and Presentations

(a) Publications

1. Li, C.-Y. and Mackenzie, J.D., "CdS-Doped Ormosils as Nonlinear Optical Materials," SPIE Proc. **1692** (1992) 211-218.

2. Li, C.-Y., Wilson, M., Haegel, N., Mackenzie, J.D., Knobbe, E.T., Porter, C., and Reeves, "Preparation on Quantum-Size Semiconductor-Doped Ormosils and their Optical Properties," Mat. Res. Soc. Symp. Proc. **272** (1992) 41-46.

3. Li, C.-Y., Tseng, J., Lechner, C., and Mackenzie, J.D., "Preparation of Metal-Cluster-Ormosil Nanocomposites," Mat. Res. Soc. Symp. Proc. **272** (1992) 133-138.

4. Tseng, J., Li, C.-Y., Takada, T., Lechner, C. and Mackenzie, J.D., "Optical Properties of Metal-Cluster-Doped ORMOSILS Nanocomposites," SPIE Proc. **1758** (1992) 612-621.

5. Yamane, M., Takada, T., Mackenzie, J.D., and Li, C.-Y., "Preparation of Quantum Dots by the Sol-Gel Process," SPIE Proc. **1758** (1992) 577-586.

6. Takada, T., Yano, T., Yasumori, A., Yamane, M., and Mackenzie, J.D., "Preparation of Quantum Size CdS-Doped Na_2O-B_2O_3-SiO_2 Glasses with High Nonlinearity," J. Non-Cryst. Solids **147/148** (1992) 631-635.

7. Li, C.-Y., Tseng, J.Y., Morita, K., Lechner, C., Hu, Y., and Mackenzie, J.D., "ORMOSILs as Matrices in Inorganic-Organic Nanocomposites for Various Optical Applications," SPIE Proc. **1758** (1992) 410-419.

8. Kao, Y.H., Hu, Y., Zheng, H., Mackenzie, J.D., Perry, K., Bourhill, G., Perry, J.W., "Second Harmonic Generation in Transparent Barium Borate Glass-Ceramics," accepted for publication, J. Non-Cryst. Solids.

9. Takada, T., Li, C.-Y., Tseng, J.Y., and Mackenzie, J.D., "Control of Particle Size Distribution of CdS Quantum Dots in Gel Matrix," paper submitted to J. of Sol-Gel Science and Technology.

10. Takada, T., Mackenzie, J.D., Yamane, M., Kang, K., Peyghambarian, N., Reeves, R.J., Knobbe, E.T., Powell, R.C., "Preparation and Nonlinear Optical Properties of CdS Quantum Dots in Na_2O-B_2O_3-SiO_2 Glasses by the Sol-Gel Technique," paper submitted to J. Opt. Soc. Am. B.

11. Wilson, M.T., Li, C.-Y., Mackenzie, J.D. and Haegel, N.M., "Photoluminescence Excitation Spectroscopy Study of CdS Nanocrystals in Ormosils, paper submitted to Nanostructured Materials.

(b) Presentations

Reeves, R.J., Powell, R.C., Knobbe, E.T., Li, C.-Y., Mackenzie, J.D., Takada,T., and Yamane, M., "Subpicosecond Degenerated Four-Wave Mixing in Sol-Gel Prepared CdS Microcrystallites," Proceedings of 1992 OSA Annual Meeting, Albuquerque, New Mexico, September (1992).

Li, C.-Y. and Mackenzie, J.D., "Ormosils as Matrices for Ultrafine Inorganic Particles," paper presented at UCLA/NSG Workshop on: **Science and Application of Photonic Materials II**, Osaka, Japan, November (1992).

Haixing, Z., and Mackenzie, J.D., "Ultrafine Particles-Glass Matrix Interactions," paper presented at UCLA/NSG Workshop on: **Science and Applicaton of Photonic Materials II**, Osaka, Japan, November (1992).

Li, C.-Y., Tseng, J.Y., Molrita, K., Lechner, C., Hu, Y., Mackenzie, J.D., "Ormosils as Matrices in Inorganic-Organic Nanocomposites for Various Optical Applications," presented at Sol-Gel Optics-II Conference, San Diego (1992).

Yamane, M., Takada, T., Mackenzie, J.D and Li, C.-Y., "Preparation of Quantum Dots by the Sol-Gel Process," presented at Sol-Gel Optics-II Conference, San Diego (1992).

Tseng, J.Y., Li, C.-Y., Takada, T., Lechner, C., Mackenzie, J.D., "Optical Properties of Metal Cluster-Doped Ormosil Nanocomposites," presented at Sol-Gel Optics-II Conference, San Diego, CA (1992).

Kang, K., Sandalphon, Y.Z. Hu, Koch, S.W., Peyghambarian, M., Li, C.-Y., Takada, T., Mackenzie, J.D., Liu, L.C., Risbud, H., "Nonlinear Optical Properties of CdS Quantum Dots Prepared by a Sol-Gel Technique: Spectral Hole Burning and Photodarkening," paper presented at the CLEO Conference, Baltimore, Maryland, May (1993).

5. Personnel

Professor J.D. Mackenzie was the Principal Investigator. External collaborators were Professor M. Yamane, Tokyo Institute of Technology and Professor N. Peyghambarian, University of Arizona. Dr. T. Takada was the Visiting Postdoctoral Scholar from the Tokyo Institute of Technology. Ms. Lisa Kao was the UCLA Ph.D. student, a U.S. national, who visited and studied with Professor Yamane in Tokyo. Mr. C.-Y. Li was a Ph.D. student working on the CdS-Ormosil materials and Ms. Justine Tseng was an M.S. student working on the metal cluster materials. In addition, Dr. Xu Yuhuan, Research Associate, has been working part-time on this project.

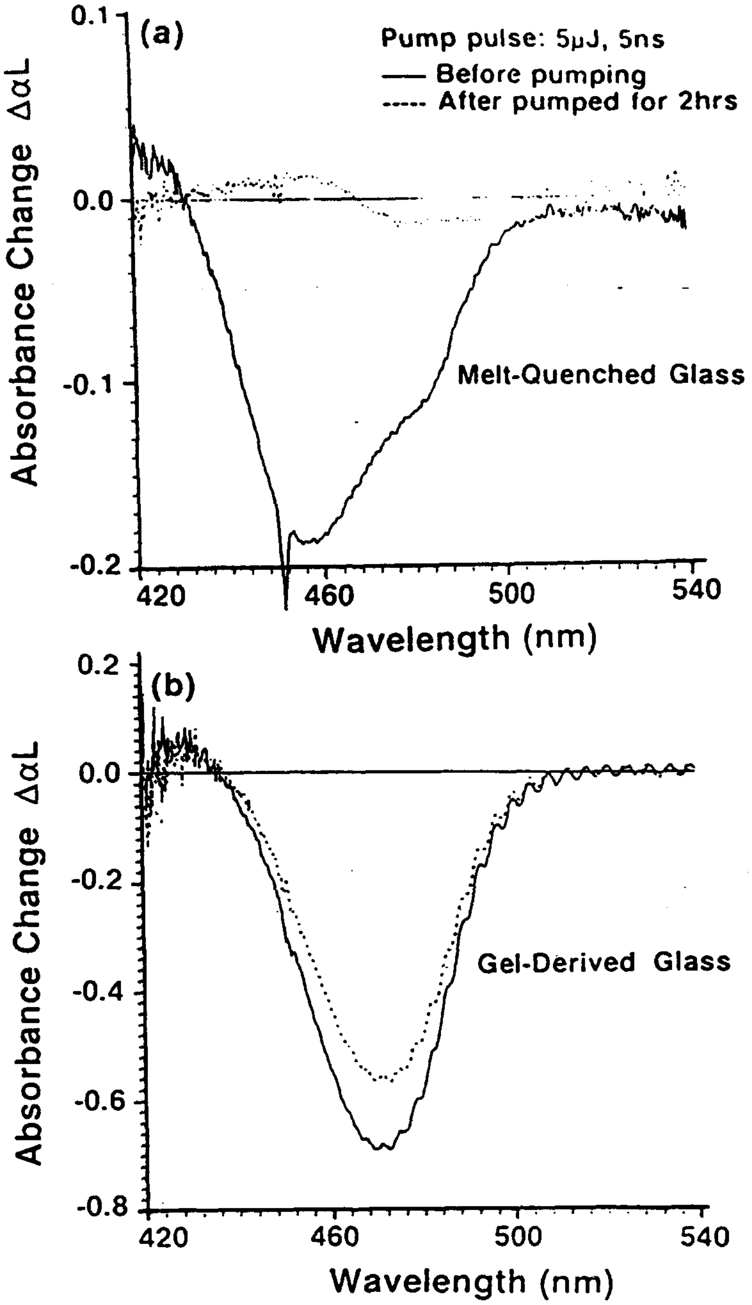

Fig. 1 Differential absorption spectra of (a) melt-quenched, and (b) sol-gel derived CdS microcrystallite doped glass sample. Solid and dashed curves are associated with $\Delta\alpha L$ spectra taken before and after extended laser exposure, respectively.

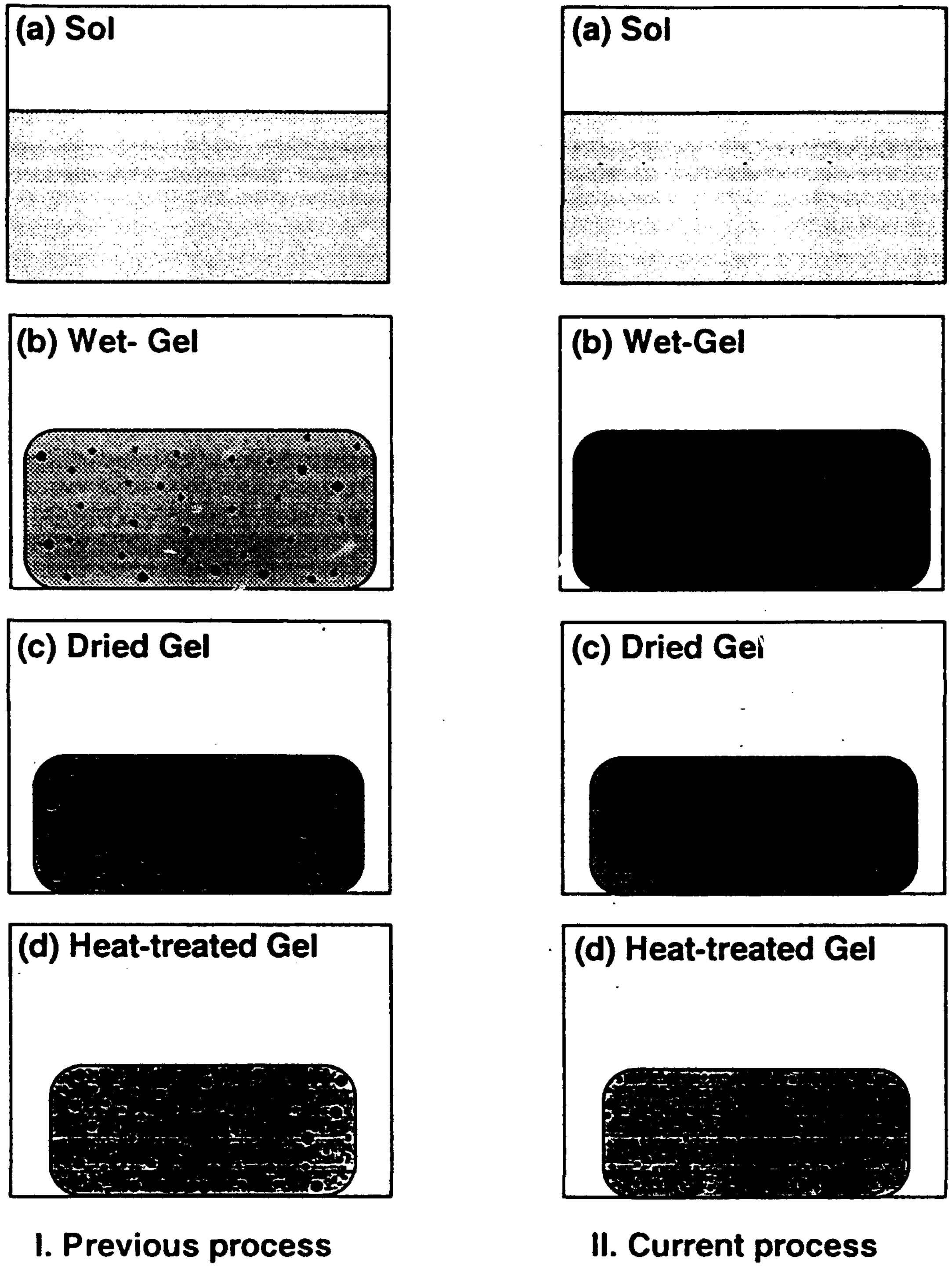

Fig. 2 Schematic illustration of the metal salt particle growth in our previous (I) and current (II) gel preparation process.

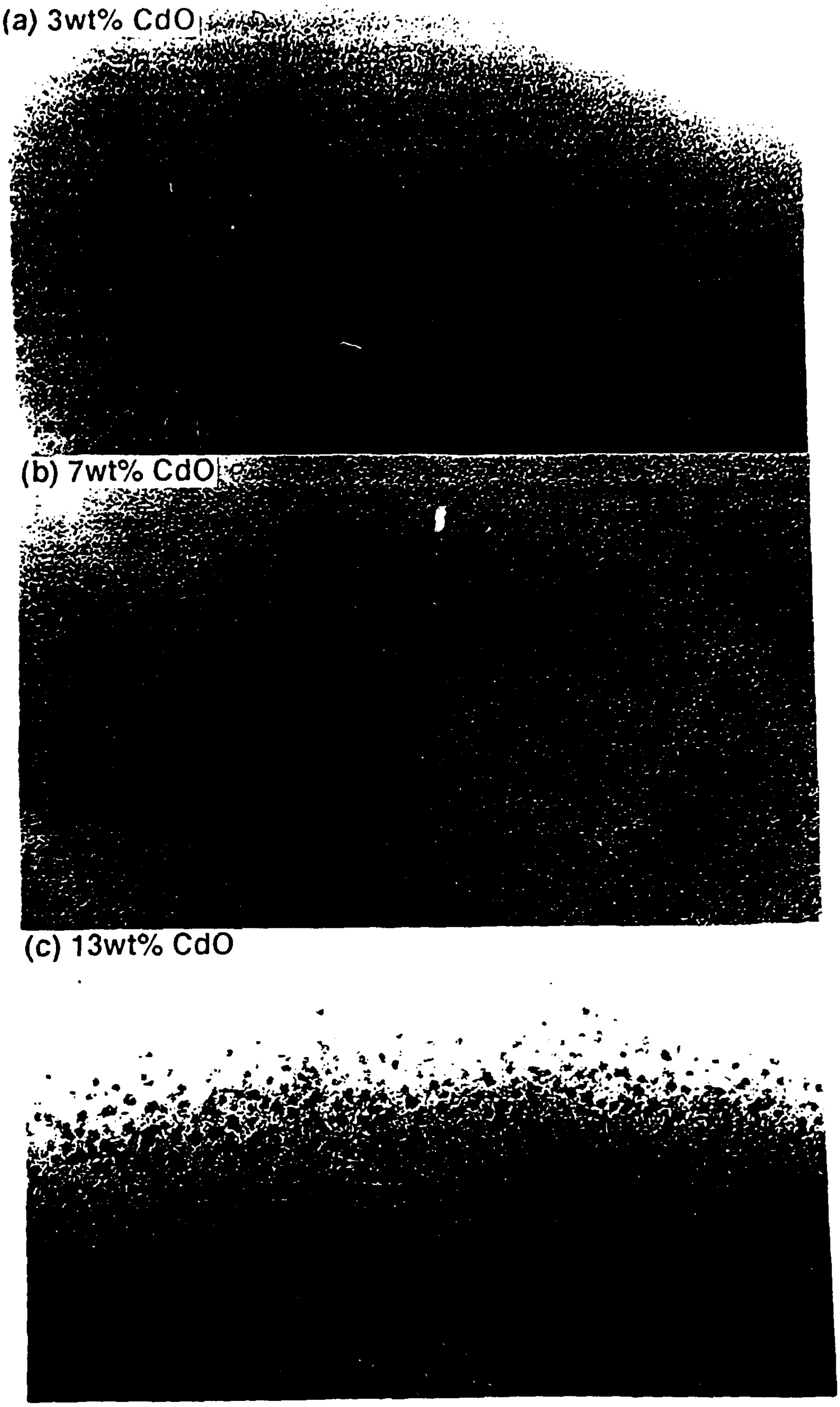

Fig. 3 TEM micrographs of CdO particles in the newly developed gels (—— 20 nm)

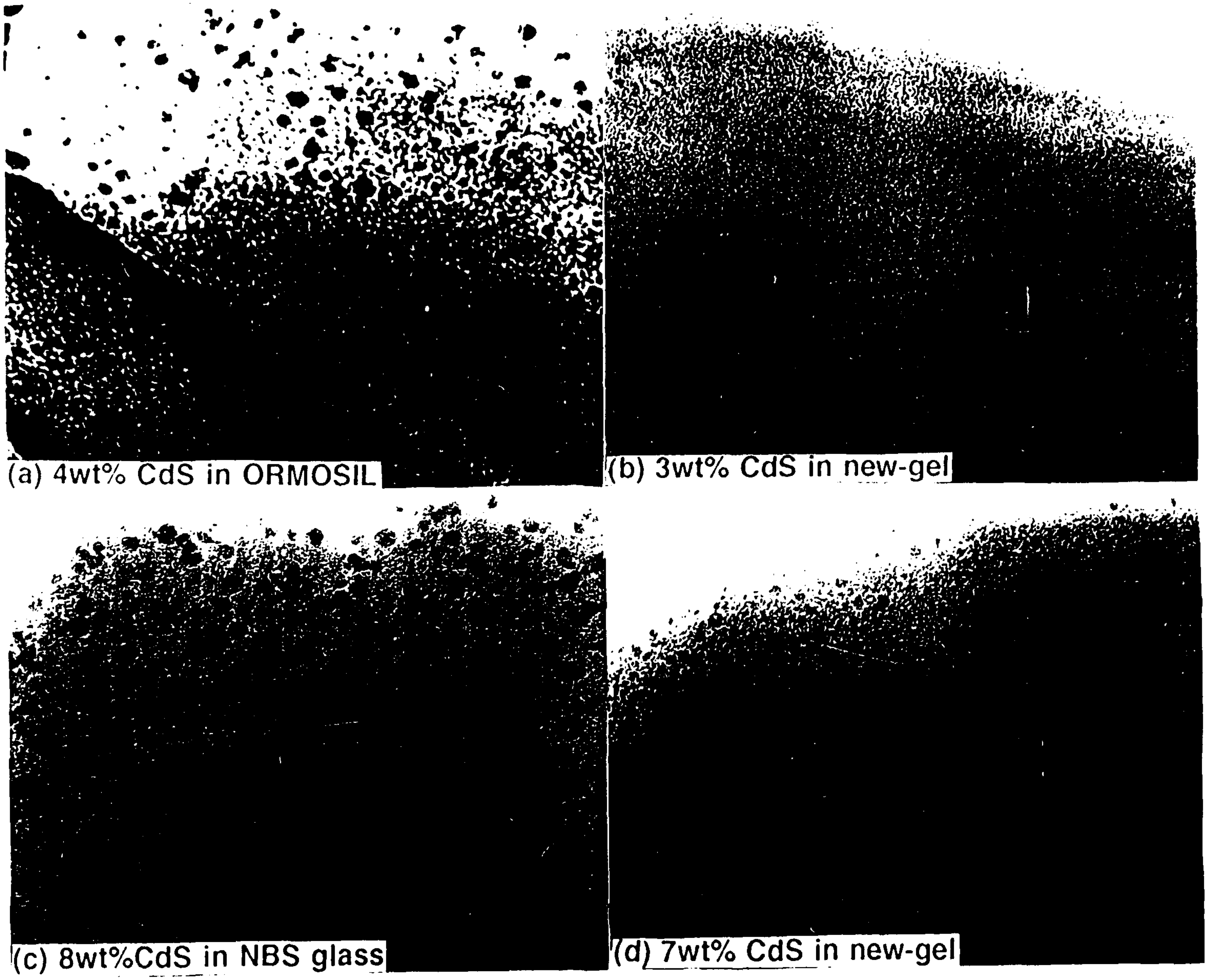

Fig. 4 TEM micrographs of CdS partgicles in the different matrices, which are (a) ORMOSIL, (b) and (d) newly developed gel, (c) Na_2O-B_2O_3-SiO_2 glass (—— 20 nm).

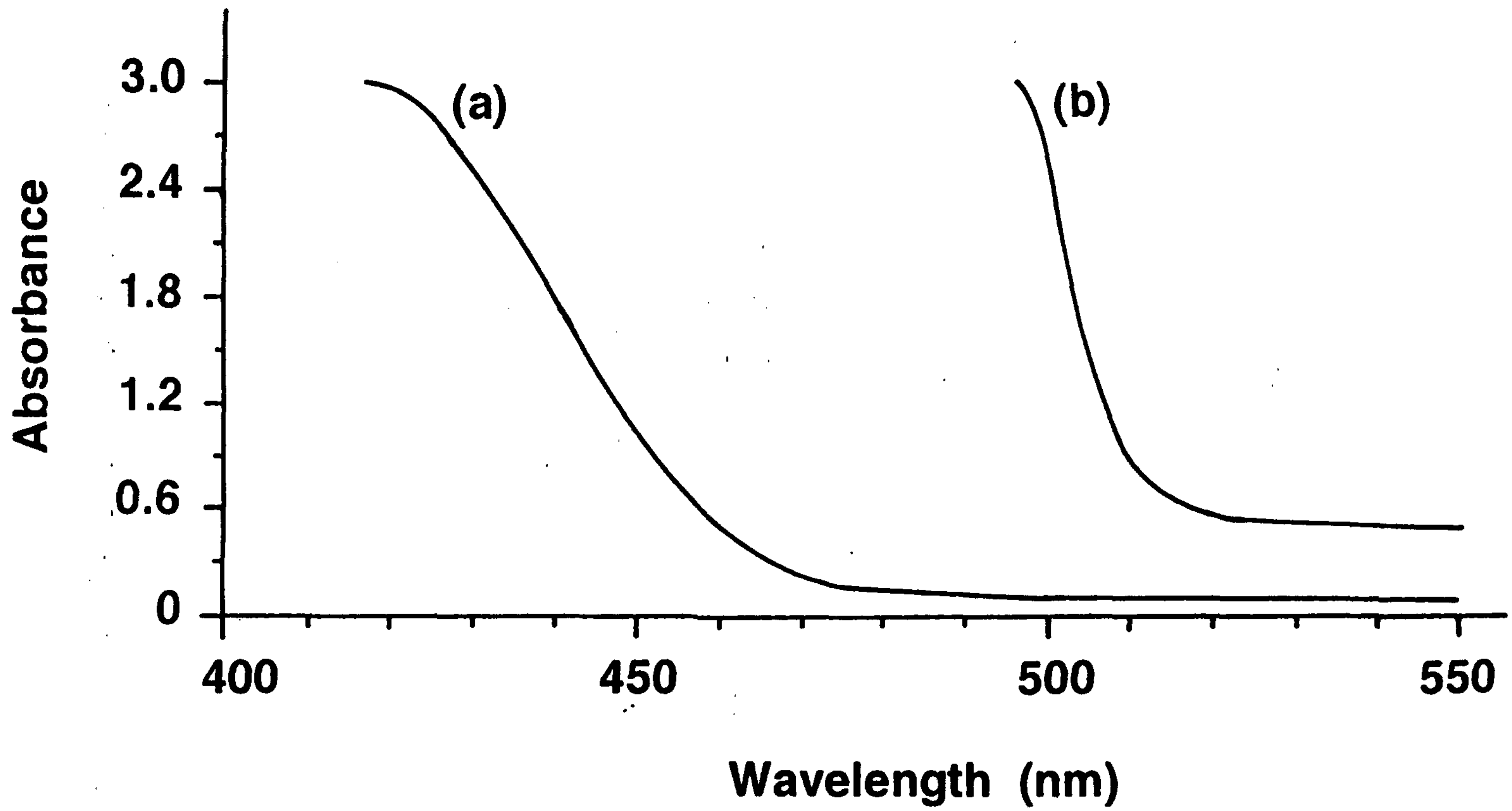

Fig. 5 Optical absorption spectra of CdS doped samples, which are:

(a) 7 wt.% CdS doped newly developed gel

(b) 8 wt.% CdS doped Na_2O-B_2O_3-SiO_2 glass

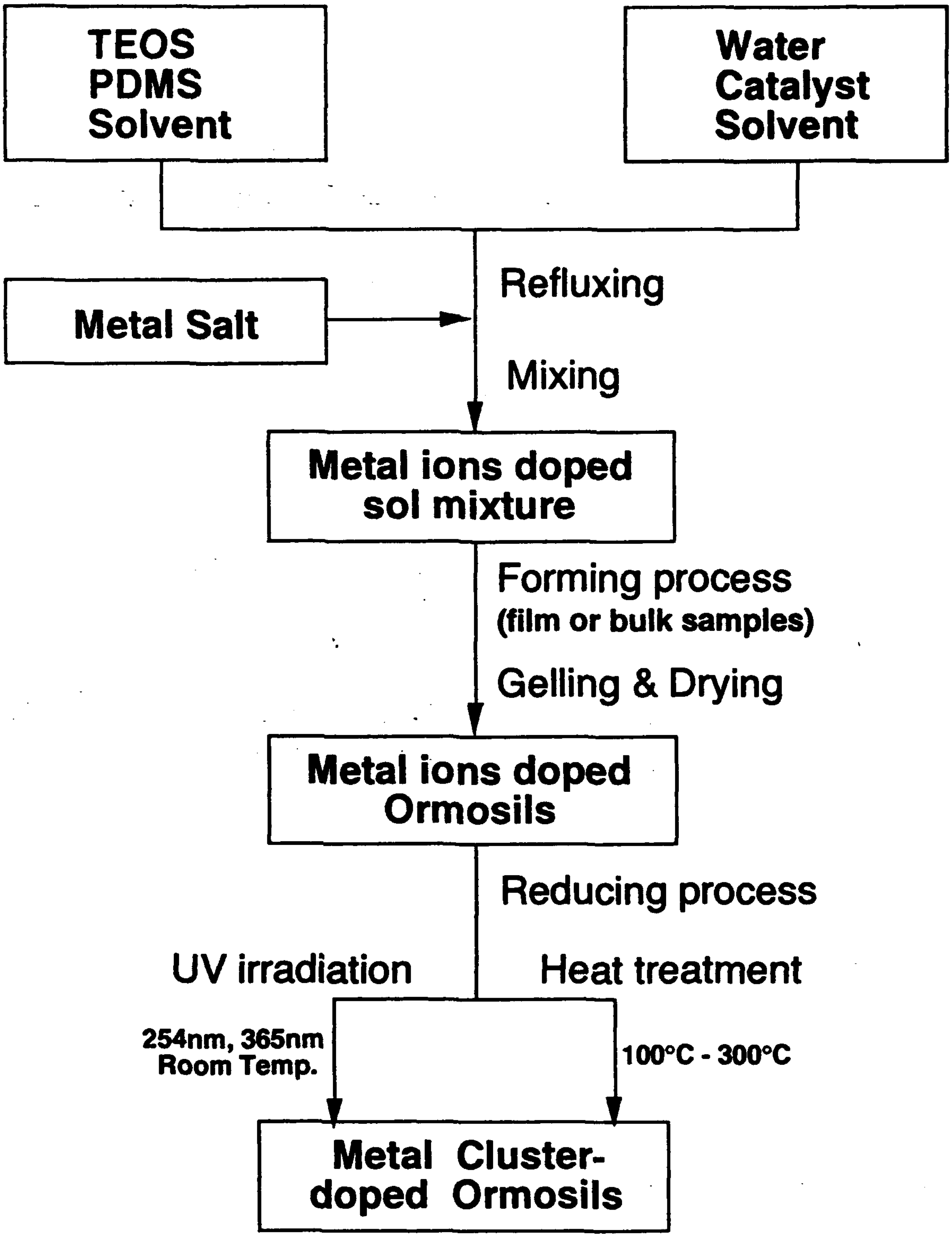

Fig. 6 Schematic process for preparation of metal cluster doped Ormosils

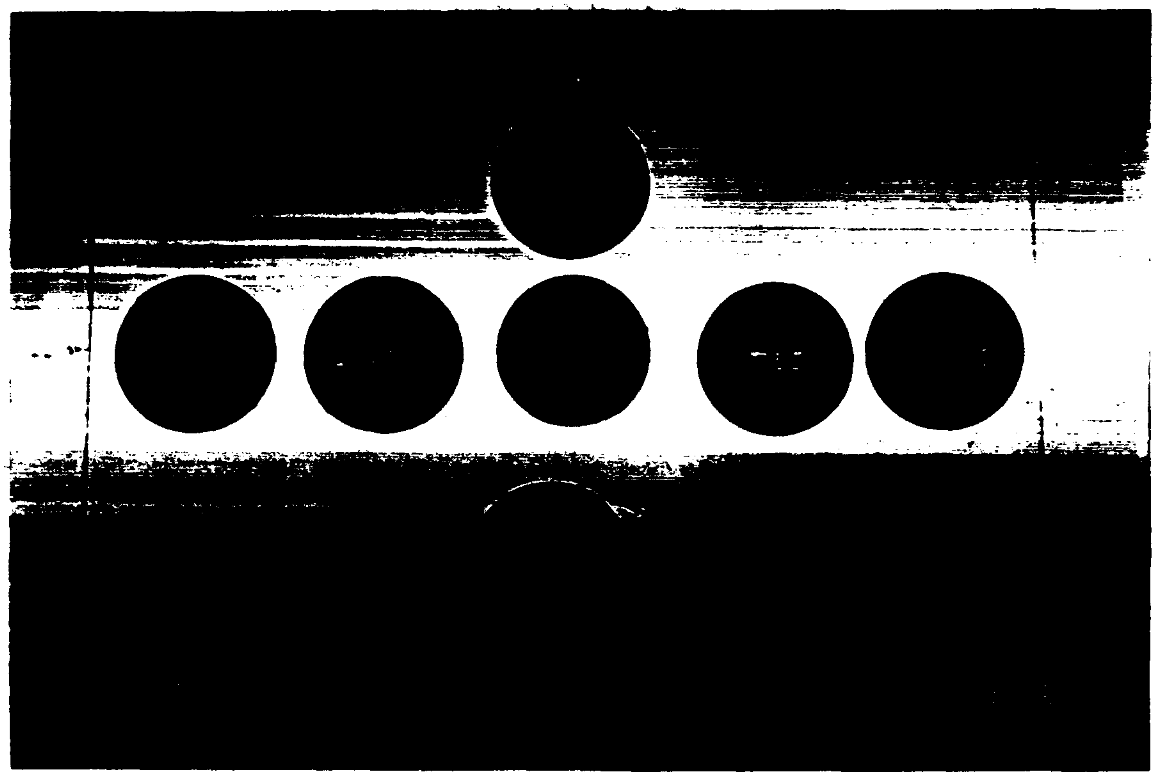

Fig. 7 Patterned Au doped Ormosils after UV irradiation